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5      COMPOSITE MATERIALS CONTAINING A NANOSTRUCTURED CARBON  
BINDER PHASE AND HIGH PRESSURE PROCESS FOR MAKING THE SAME

Related Application

10      The present Application claims the benefit of U.S. Provisional Application No.  
60/457,445, filed March 26, 2003, entitled "DIAMOND-BONDED COMPOSITES  
AND METHOD FOR PRODUCTION OF SAME."

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N00014-01-1-0079 both awarded by the Office of Naval Research; by the terms of  
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Agency; and by the terms of Contract No. DAAH01-OO-CR008 funded by U.S. Army Aviation and Missile Command.

#### Field of the Invention

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The present invention relates generally to composite materials containing a nanostructured carbon binder phase, and more particularly to composite materials containing a matrix phase interspersed with a nanostructured carbon binder phase, and to a pressure-sintering process for making the same.

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#### Background of the Invention

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Research in advanced composite materials has yielded a substantial range of remarkable and diverse products. Advanced composite materials typically exhibit properties including high strength and high stiffness, low weight, corrosion resistance, and even special electrical properties in certain materials. The combination of properties have made advanced composite materials useful for various applications including aircraft and aerospace structural parts, exhaust systems, machine tools, armor plates, chemical- and heat-resistant protective coatings, and the like.

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Composite materials are grouped generally into three basic groups depending on the corresponding matrix phase composed of a material selected from polymers,

metals, and/or ceramics. Manufacturing and sale of composite materials represent a multi-billion dollar industry that provides a range of materials for products from high performance sports equipment to aerospace components. A common composite material is the carbon/carbon composite, which is typically composed of a matrix  
5 phase comprising carbon fibers and a binder phase in the form of a graphitized resin for providing strength and rigidity. These composites represent special materials that exhibit high specific strength and toughness, while providing good resistance to heat. These materials can be suitably used in high temperature applications such as, for example, heat shields for re-entry vehicles, braking components, radiators  
10 and heat sinks.

Such carbon composites typically can be made either through standard impregnation processes or chemical vapor infiltration (CVI) processes. The impregnation process typically takes preforms of carbon fibers, impregnates them  
15 with resin or pitch, followed by carbonization and graphitization. Both the impregnated resin and pitch shrink during the carbonization and graphitization steps, necessitating several cycles of impregnation and carbonization to obtain dense carbon composites. The carbonization and graphitization process is typically carried out through pyrolysis (chemical change via heating) of the resin at relatively high  
20 temperatures, for example, in the range of from about 500°C to 3,000°C depending on the corresponding process implemented.

The chemical vapor deposition process has become one of the most common processes for fabricating carbon composites. The main disadvantages of this process are long processing times (500 to 600 hours), the presence of closed porosity, low strength, broad density gradients, and the need to machine the outer impermeable skin from the composite to facilitate infiltration. Accordingly, the processes used to fabricate the composite materials can be both expensive, labor intensive and time-consuming to carry out.

Accordingly, there is a need to develop a composite material that exhibits enhanced structural properties over the composites described in the prior art while substantially reducing the time and cost needed for production. It would be highly desirable to develop a composite material containing a matrix phase interspersed with a nanostructured carbon binder phase, wherein the matrix phase can be composed of a material such as a ceramic, a metal, or combinations thereof. There is a further need for a process of fabricating such composite materials using existing reagents and equipment commercially available and which can be performed in an environmentally compatible, cost efficient and simple manner.

#### Summary of the Invention

The present invention is directed generally to composite materials and process for making the same. The composite materials of the present invention exhibit desirable properties including high strength and low weight, and are simpler

and more cost efficient to fabricate than composite materials possessing similar properties. The processes of the present invention have been found to afford considerable flexibility in tailoring the properties of the resulting composite materials to meet the performance requirements of a range of applications, such as rocket parts, exhaust systems, aerospace structures, machine tools, armor plates, and protective coatings. The composite materials of the present invention can be in the form of, for example, particle-strengthened materials, fiber-strengthened materials, network-strengthened materials, and bi-/tri-continuous-strengthened materials.

10       The composite materials of the present invention are generally composed of a matrix phase or preform selected from materials such as ceramics, metals or combinations thereof, with a nanostructured carbon binder phase interspersed throughout the matrix phase to provide strength and ensure the integrity of the resulting material. The nanostructured carbon binder phase is derived from a carbon binder mixture substantially composed of carbon nanoparticles. A pressure-assisted sintering process is used to distribute and uniformly infuse the carbon binder mixture into the matrix phase, which the resulting combination is thereafter sintered to polymerize the carbon binder mixture and yield a nanostructured carbon binder phase. The carbon nanoparticles used in the present invention may be selected from fullerenes and mixtures thereof.

Upon pressure-assisted sintering, the resulting composite material containing the newly formed nanostructured carbon binder phase exhibits high specific strength

and toughness, low weight and good thermal stability, while imparting resilience to the material. The fabrication process requires a relatively short period of time to complete. Optionally, the carbon binder mixture can further contain other forms of carbon including, for example, pitch carbon, anthracite carbon, diamond, graphite, carbon fibers, and the like. The other forms of carbon can be present in the carbon binder mixture in amounts ranging from about 1.0% to 99% weight based on the total weight of the carbon binder mixture.

The composite materials of the present invention exhibit advantages including relative ease in sufficiently infiltrating the open pore space of the matrix phase or preform, relatively short processing time, flexibility in control of bonding between the matrix phase and the nanostructured carbon binder phase, and process scalability at economical cost.

In one aspect of the present invention, there is provided a composite material, which comprises a matrix phase having a nanostructured carbon binder phase derived from a carbon binder mixture comprising mixed fullerenes, interspersed throughout the matrix phase.

In another aspect of the present invention, there is provided a method of making a composite material which comprises the steps of:

dispersing a sufficient amount of carbon binder mixture comprising mixed fullerenes, into a matrix phase; and

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applying sufficient sintering pressure to the carbon binder mixture and the matrix phase at a sintering temperature for a sufficient time to form a nanostructured form of carbon, whereby the composite material is obtained.

5        The immediately previous method may, prior to the applying step, further include the step of applying a sufficient dispersing pressure to the carbon binder mixture and the matrix phase at a dispersing temperature for a sufficient time to facilitate diffusion or dispersal of the carbon nanoparticles throughout the matrix phase.

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#### Brief Description of the Drawings

Various embodiments of the invention are described in detail below with reference to the drawings, in which like items are identified by the same reference  
15    designations, wherein:

Figure 1 is a schematic representation of a particle-strengthened composite showing the arrangement of matrix phase particles to carbon binder phase for one embodiment of the present invention;

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Figure 2 is a schematic representation of a fiber-strengthened composite showing the arrangement of matrix phase fibers to carbon binder phase for a second embodiment of the present invention;

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Figure 3 is a schematic representation of a network-strengthened composite showing the arrangement of a matrix phase wires to carbon binder phase for a third embodiment of the present invention;

5        Figure 4 is a schematic representation of a bicontinuous-strengthened composite showing the arrangement of a porous or sponge-like matrix phase to carbon binder phase for a third embodiment of the present invention;

10        Figure 5A is a schematic diagram of a high pressure-high temperature (HPHT) system suitable for use in preparing the composite materials of the present invention;

15        Figure 5B is an exploded detailed cross sectional view of an anvil pair and support rings assembly of the HPHT system shown in Figure 5A;

      Figure 5C is an exploded detailed cross sectional view of a reaction cell defined by the anvil pair and support rings assembly shown in Figure 5B;

20        Figure 6A is a representative micrograph of the surface of a hardened steel sample with hardness indentations of various loads embossed thereon;



Figure 6B is a representative micrograph of the surface of a composite material of the present invention with hardness indentations of various loads embossed thereon; and

5        Figure 7 is a graph showing compressive stress-strain curves which indicate increase in strength and stiffness with volume fraction of diamond while fracture strain remains at about 2%.

#### Detailed Description of the Invention

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The present invention is generally directed to a composite material produced from a starting material composed of a matrix phase in combination with a carbon binder mixture comprising carbon nanoparticles. The starting material is thereafter treated under suitable conditions to polymerize the carbon nanoparticles into a  
15    carbon binder phase comprising a relatively hard nanostructured carbon material, thereby yielding the composite material of the present invention. The treatment comprises a pressure-assisted sintering process that is carried out under elevated pressure at an elevated temperature for a sufficient time to induce the carbon nanoparticles to polymerize. The resulting composite material exhibits high  
20    hardness, compressive strength and stiffness, and enhanced fracture resistance, which has been found to correspond to the cohesive strength of the interphase interfaces in the composite material. The approach of the present invention affords considerable flexibility in tailoring the properties of the novel composite materials to

the performance needs of various applications, such as rocket parts, exhaust systems, aerospace structures, machine tools, armor plates, and protective coatings. The composite materials of the present invention can readily be fabricated in a cost effective manner using conventional commercially available equipment and  
5 materials.

In a particular aspect of the present invention, there is disclosed a new class of composite materials, including particle-, fiber-, and network-, bi-/tri-continuous-strengthened forms (see Figures 1 through 4, respectively) comprising an  
10 interspersed, high hardness, nanostructured carbon binder phase acting as a binder material. The materials are produced by combining or infiltrating a porous matrix phase with a carbon binder mixture containing carbon nanoparticles (i.e., fullerenes and combinations thereof), followed by a pressure-assisted sintering process to transform the carbon nanoparticles into the desired nanostructured carbon binder  
15 phase. The matrix phase may be selected from a range of materials, including but not limited to, metals, ceramics, carbon-based compounds, silicon-based compounds, glass, carbides, nitrides, borides, oxides, and the like.

The metals can include iron, nickel, cobalt, titanium, aluminum, beryllium,  
20 copper, silver, gold, platinum, tungsten, molybdenum, uranium, and the like, and alloys thereof. The ceramics can include carbides, nitrides, silicides, oxides, silica, alumina, zirconia, yttria, magnesia, beryllia, titanium carbide, beryllium carbide, boron carbide, boron nitrides, silicon carbide, silicon nitride, titanium boride,

tungsten carbide, uranium carbide, and the like, and mixtures thereof. The amount of matrix phase present in the composite material can range from 1 to 99% by weight based on the total weight of the composite material.

5           An example of parameters applicable for the sintering process include a pressure ranging from a pressure of at least 0.1 GPa, preferably from about 0.1 GPa to 10.0 GPa, and more preferably from about 0.1 to 1.0 GPa at a sustained temperature of at least 400°C, preferably from about 400°C to 1000°C, with processing times of from about 100 to 10,000 seconds. Applicants have found that  
10   sintering a carbon binder mixture comprising fullerenes at a pressure of about 1.0 GPa and a temperature of about 800°C yielded a nanostructured carbon binder phase exhibiting a hardness level comparable to silicon carbide, while sintering the carbon binder mixture comprising fullerenes at a pressure of about 0.1 GPa and a temperature of about 1000°C yields a nanostructured carbon binder phase exhibiting  
15   a hardness level comparable to steel.

          The term “carbon nanoparticles” is used to encompass a class of carbon substantially spherically shaped particles of from about 0.71 to 20 nm size, so called fullerenes, such as, for example, C<sub>60</sub>, C<sub>70</sub>, C<sub>120</sub>, and the like, and mixtures thereof. A  
20   “fullerene” is a form of carbon composed of clusters of sixty carbon atoms (C<sub>60</sub>) or more bonded together in a polyhedral structure composed of pentagons and hexagons. A “nanotube” is a form of carbon composed of cluster of carbon bonded together in a substantially cylindrical structure with a diameter of a few nanometers.

Carbon nanoparticles particularly fullerene ( $C_{60}$ ) can be crystallized into a face-centered cubic structure to yield fullerite, which is generally a black crystalline solid, soluble in toluene, for example. This form or phase of carbon is thermodynamically unstable at high pressure and temperature, and tends to convert to a different form of carbon. When fullerenes and nanotubes are consolidated in the presence of moderate to high pressure and elevated temperature, they form into a nanostructured form of carbon exhibiting a hardness value comparable to silicon carbide, and at higher pressures, exhibiting a hardness value comparable to diamond.

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Carbon nanoparticles (i.e., fullerenes, nanotubes, and the like) can be readily produced by inducing an electric arc struck between graphite electrodes in the presence of an inert atmosphere contained within a water-cooled chamber. The electric-arc method of producing  $C_{60}$  also yields a smaller number of fullerenes such as  $C_{70}$ ,  $C_{76}$ ,  $C_{78}$ ,  $C_{84}$ ,  $C_{90}$ , ...  $C_{120}$ , and similar higher number carbon compounds, which have less symmetrical molecular structures. The soot-like product consists of a mixture of graphite particles and carbon nanoparticles (i.e., fullerenes, nanotubes, and the like). Generally, the carbon nanoparticles can be readily separated from the larger graphite particles by placing the mixture into a suitable liquid hydrocarbon solvent such as toluene, which is able to dissolve the carbon nanoparticles while leaving the larger graphite particles solid and intact. As the carbon nanoparticles solubilize into the solvent (e.g., toluene), the larger graphite particles settle out. The solution can then be filtered to remove the graphitic particles and the dissolved

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carbon nanoparticles can then be extracted from the filtrate. Further separation can be optionally accomplished through liquid chromatography techniques as known in the art.

5           The terms “pressure sintering” or “pressure-assisted sintering” refer generally to the process of heating and compacting a material at relatively high pressure at a temperature below its melting point to weld discrete components (i.e., matrix phase and carbon binder mixture) together to yield an intact rigid composite material of the present invention as disclosed hereinafter.

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          As discussed above, current practice for fabricating composites containing a carbon-based packing material have been implemented typically through the use of chemical vapor infiltration (CVI) of preforms or matrix phase. Although CVI has been proven to be a reliable technology, the CVI process, which is only capable of  
15   producing graphite, is relatively slow and labor intensive which may require several days to complete. Additionally, problems including uneven densification of the carbon infiltrant and closed porosity of the preform, which adversely affects the mechanical properties of the final product, are typically associated with the CVI process. To overcome the limitations of the prior art, Applicants have investigated a  
20   novel approach of infiltrating preforms with carbon nanoparticles selected from fullerenes, and the like, and combinations thereof. Carbon nanoparticles have the capability due largely in part to their molecular dimensions to fill and occupy open porosity in the preform. Upon infiltration, the carbon nanoparticles are transformed

through pressure-assisted sintering into a hard and tough carbon binder phase in bonded association with the preform to readily yield the composite material of the present invention.

5           Accordingly, a feature of the processing route described herein is the use of carbon nanoparticles (i.e., fullerenes) as one of the starting materials for processing through pressure-assisted sintering, or hot pressing. Subsequently, during hot pressing, it is believed that the simultaneous application of high pressure and temperature, acting on the carbon nanoparticles, is the key to the formation of the  
10 nanostructured carbon binder phase. In addition to the corresponding pressure and temperature conditions, the holding time, which must be sufficient to enable completion of the sintering process, involving cross-linking of the carbon nanoparticles (i.e., fullerenes) to form a nanostructured form of carbon referred herein as the "carbon binder phase." Applicants hypothesize that the high hardness  
15 displayed by the nanostructured carbon binder phase is due to the formation of mixed  $sp^2$  and  $sp^3$  bonds in the cross-linked structure, with a preponderance of  $sp^3$  bonds, while surprisingly retaining the resilience of a polymer-based material.

          Pressure-assisted sintering for producing the composite materials of the  
20 present invention can be accomplished in several ways. When sintering pressure is less than 0.3 GPa, the present composite materials can be fabricated by conventional hot isostatic pressing (HIP) technology. For pressures greater than 0.3 GPa, it is preferable to utilize a uniaxial-type of hot pressing unit, which are widely

known in the art. For those skilled in the art, it will be recognized that scaling present high-pressure technology to fabricate large flat panels or massive monolithic pieces can be readily accomplished.

5           Applicants have discovered that carbon nanoparticles such as a mixture of fullerenes can be pressure sintered in relatively large volumes at a pressure of at least 0.1 GPa, preferably ranging from about 0.1 to 10.0 GPa, and at a temperature of, for example, from about 400°C to 1000°C, to yield the desired novel nanostructured carbon binder phase exhibiting physical properties on a scale  
10   between graphite and diamond.

          Prior to pressure sintering the matrix phase containing the carbon binder mixture, the carbon binder mixture can be infiltrated into the matrix phase by applying a sufficient infiltration pressure at a suitable elevated temperature to  
15   enhance the fluidity of the mixture, and thus better facilitating the even penetration of the carbon binder mixture into the matrix phase. By applying the sufficient infiltration pressure and elevated temperature, the carbon nanoparticles has been found to readily infiltrate and permeate through the pores and spaces within the matrix phase. The infiltration pressure is generally at least 0.01 GPa, and preferably from about  
20   0.01 GPa to 0.1 GPa and the elevated temperature is generally at least 20°C, preferably from about 20°C to 100°C, depending on the desired achievement of the viscosity of the carbon binder mixture formed from carbon nanoparticles, and optional additional carbon material or compounds which can be carbonized or

graphitized. The additional carbon material can be aromatic hydrocarbons, diamond, graphite, amorphous, nanotubes, and the like. Such aromatic hydrocarbons can be coal-tar pitch, petroleum pitch, anthracene, naphthalene and the like, and mixtures thereof.

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In one embodiment of the present invention, the novel nanostructured carbon binder phase exhibits a hardness of at least four on the Mohs scale, and more specifically from about four to nine on the Mohs scale. The novel nanostructured carbon binder phase further exhibits an apparent density of from about 1.6 to 2.3 g/cm<sup>3</sup>, and a resistivity in the range of from about 0.1 to 1.0 ohm · cm. Furthermore, the nanostructured carbon binder phase exhibits a resilience of at least 2% strain to fracture, which is a surprising characteristic for a material of such relative hardness.

In the present invention, the carbon nanoparticles, including fullerenes, and the like, and mixtures thereof, are utilized as infiltrants in the fabrication of the novel composite materials of any form including, but not limited to, particle-strengthened composites, fiber-strengthened composites, network-strengthened composites and bi-/tri-continuous-strengthened composites. Carbon nanoparticles are excellent infiltrants due in part to their desirable small molecular dimensions, and their capacity to fill all open porosity of the corresponding matrix phase, whatever size and shape. The composite materials of the present invention are fabricated by pressure sintering the carbon nanoparticle infiltrated preform or matrix phase to yield the composite material of the present invention. In a preferred embodiment, the carbon



binder mixture used to produce the carbon binder phase upon pressure sintering, comprises mixed fullerenes. The term "mixed fullerenes" means a mixture of fullerenes of varying molecular weights. The use of mixed fullerenes yielded an unexpected result in providing a carbon binder phase that can be used at lower  
5 pressures compared to using highly pure  $C_{60}$ , for example. Such use of mixed fullerenes also substantially lowers the cost for fabricating the composite material.

With reference to Figure 1, a composite material in the form of a particle-strengthened composite 1 is shown for one embodiment of the present invention.  
10 The particle-strengthened composite 1 is derived from a starting material composed of a powder matrix phase made up of matrix particles 2 such as, for example, powder forms of metals, ceramics, carbides including boron carbide, silicon carbide, titanium carbide, and the like, or borides including titanium boride, or nitrides including cubic-boron nitride, and the like, or diamond, and a carbon binder mixture 4  
15 comprising carbon nanoparticles including, for example, fullerenes and/or nanotubes having sizes in the range of from about 0.7 nm to 20 nm. The particle-strengthened composite 1 is produced by mixing the matrix particles 2 of the powder matrix phase and the carbon binder mixture 4, and treating the starting material via pressure sintering under conditions described above to cause the carbon binder mixture 4 to  
20 polymerize and form into a hard nanostructured carbon binder phase. The particle-strengthened composite 1 exhibits relatively high hardness levels and excellent wear resistance.

Note that for the description of Figure 1, and the following description relative to Figures 2 through 4, that the Figures themselves are not meant to convey actual geometric shapes, but are simplistic views for purposes of illustration only.

5           Applicants have discovered that wear resistance can be enhanced by increasing the weight ratio of matrix particles 2 relative to the carbon binder mixture 4. In one preferred embodiment, the matrix particles 2 are present in amount of about 60% by weight of the starting material. Particle-strengthened composites 1 of the present invention exhibit high hardness and wear resistance, particularly those  
10   containing a high fraction of uniformly dispersed superhard matrix particles such as diamond or cubic-boron nitride. Applicants also note that the strength of the particle-strengthened composite 1 can be further enhanced by blending matrix particles 2 of varying grades or sizes to formulate the matrix phase into a high weight fraction mixture. The use of varying grades of particles 2 functions to greatly increase the  
15   packing density or solids loading of the mixture. Such particle blending is a common practice in the ceramic industry. The selection of proper grade mixtures suitable for producing particle-strengthened composites 1 with the desirable strength characteristics can readily be determined and modified by the skilled artisan in the art.

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Referring to Figure 2, a composite material in the form of a fiber-strengthened composite 5 is shown for a second embodiment of the present invention. The fiber-strengthened composite 5 is derived from a starting material composed of a fiber

matrix phase composed of fibers 6 which may be in the form of chopped fibers, fabrics or three-dimensional woven structures, for example, and made from metals, ceramics, or combinations thereof; and a carbon binder mixture composed of carbon nanoparticles. The fibers 6 preferably exhibit high specific strength and can be  
5 selected from materials including carbon, silicon carbide, borocarbide, silicon oxide, alumina, and the like. The carbon binder mixture 4 is interspersed between the fibers 6 through infiltration under an infiltration pressure of from about 0.01 GPa to 0.1 GPa. The starting material is thereafter exposed to pressure sintering under conditions described above to yield the fiber-strengthened composite 5.

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Referring to Figure 3, a composite material in the form of a network-strengthened composite 7 is shown for a third embodiment of the present invention. The network-strengthened composite 7 is produced from a starting material comprising a matrix phase generally in the form of a rigid lattice structure formed  
15 from wires 8 made from a material selected from metals, ceramics and combinations thereof, and a carbon binder mixture. The wires 8 are preferably composed of a metal selected from nickel, titanium, iron, tungsten, copper and the like, and alloys thereof. The carbon binder mixture 4 occupies and fills the spaces between the wires 8 of the lattice structure. The starting material is generally formed by infiltrating  
20 or packing the lattice structure with the carbon binder mixture 4 in an amount sufficient to provide a uniform densification therethrough. The infiltration process is facilitated by exposing the carbon binder mixture 4 to an infiltration pressure of from about 0.01 GPa to 0.1 GPa. In another embodiment, the lattice structure is under

tension during the infiltration of the carbon binder mixture 4. Once the infiltration is completed, the starting material is pressure sintered under conditions described above to change the carbon nanoparticles into the nanostructured carbon binder phase to yield a pre-stressed network-strengthened composite 7.

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Referring to Figure 4, a composite material in the form of a bi-/tri-continuous-strengthened composite 9 is shown for a fourth embodiment of the present invention. The bi-/tri-continuous-strengthened composite 9 can contain two or three continuous phases. In the latter, an interlayer is formed between the matrix phase and the carbon binder mixture through a reaction between both. Thus, the matrix phase can be composed of a suitable material capable of reaction with the carbon binder mixture during pressure sintering to yield a resulting by-product material and form a tri-continuous composite material. An example of materials capable of forming the interlayer is titanium (i.e. matrix phase) and carbon (i.e. carbon binder mixture). The bi-/tri-continuous-strengthened composite 9 is produced from a starting material comprising a porous structure 10 such as, for example, a porous ceramic, metal or combinations of both, which may be formed from partial sintering of nanoscale or microscale particles, and a carbon binder mixture 4 infiltrating the spaces within the porous structure 10 in amounts sufficient to yield a uniform densification therethrough. The infiltration process is facilitated by exposing the carbon binder mixture to an infiltration pressure of from about 0.01 GPa to 0.1 GPa. The infiltrated porous structure is thereafter treated via a pressure sintering process to convert the carbon nanoparticles in the carbon binder mixture 4 into a hard nanostructured

carbon binder phase to yield the bi-/tri-continuous-strengthened composite 9. The resulting bi-/tri-continuous-strengthened composite 9 exhibits near isotropic properties due in part to the multiple phases co-extending in three-dimensional orientations.

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In an alternative embodiment, Applicants note that both oxide and non-oxide porous ceramics, including pure compounds and their composites, can be processed to form the porous matrix structures. Applicants further note that certain ceramic materials, particularly oxide-based ceramics, have been found to react with the nanostructured carbon binder phases to yield a thin reaction layer of graphitic carbon. This thin layer of graphitic carbon located between the oxide-based ceramic and the nanostructured carbon binder phase has been found to enhance resistance to fracture. This ensures sufficient bond strength between the carbon binder phase and the matrix phase to provide effective load transfer therebetween, thus minimizing debonding at the tip of an advancing crack. In this manner, fractures can be halted at the point of origin. The increased fracture resistance is realized due to the stretched fibers exerting closure forces on the fractured portions and thus reduces the average stress intensity at the crack tip, and greatly minimizing or halting propagation of the original fracture.

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In another embodiment of the present invention, the porous structure 10 can be in the form of a porous graphitic carbon which would greatly benefit in terms of material properties from infiltration of a carbon binder mixture 4 containing carbon

nanoparticles and pressure sintering. The porous graphitic carbon can be produced by an arc-plasma method, or by carbonization of pitch into a coke sponge, as known to one skilled in the art, for example. Further, carbon nanoparticles can also be infiltrated into porous preforms or matrix phases of ceramic materials, including alumina, boron carbide, titanium boride, and the like, and then transformed by pressure-assisted sintering into bicontinuous-strengthened composite materials.

Samples of consolidated diamond powder containing a hard nanostructured carbon binder phase were prepared by sintering at a pressure of from about 0.1 to 3.0 GPa and at a temperature of from about 400°C to 1000°C, with a holding time of up to about 10,000 seconds to yield a sintered product. At a pressure of about 3 GPa and temperature of about 800°C, the sintered product exhibited a hardness of about ten on the Mohs scale.

Samples of consolidated graphitic fiber containing a combination of graphitic fibers and a hard nanostructured carbon binder phase were prepared by sintering at a pressure of from about 0.1 GPa to 0.3 GPa, and at a temperature of from about 800°C, with a holding time of up to about 10,000 seconds to yield a sintered product. The hard nanostructured carbon binder phase exhibited a hardness value similar to steel. Because of its scalability, using conventional hot pressing technologies, the pressure range 0.1 GPa to 0.3 GPa is preferred.

Figure 5A shows a schematic example of a high pressure-high temperature system 19 suitable for preparing the composite materials of the present invention. The system 19 includes a frame 22 housing a hydraulically driven working cylinder and ram assembly 26. The frame 22 further retains a container 36 having a reaction cell 37, which is supported by an anvil and supporting ring assembly 38, providing a high pressure unit 38 operatively engaged to the cylinder and ram assembly 26 through inserts 28. The reaction cell 37 is adapted to hold the materials used to make the composite material of the present invention. The cylinder and ram assembly 26 generates the necessary force on the high pressure unit 38 to compress container 36. The container 36 comprises a clay-sand mixture or a suitable electrically non-conductive material, and the reaction cell 37. An electrical current is supplied to the reaction cell 37 via a power supply 39 to generate the heat energy needed to raise the temperature of the reaction cell 37. An insulating layer 29 is provided between the frame 22 and the cylinder and ram assembly 26 for electrical insulation.

The cylinder and ram assembly 26 further includes an oil pump 24 and a pump motor 23 for supplying the hydraulic movement. The high pressure high temperature system 19 further includes electronic control devices such as a multimeter 21, a controller 25, a multimeter 30, an electrical shunt 31, an oil pressure gauge 32, a computer 35, an electrical valve 27, and a secondary oil pump motor 33 for powering a secondary oil pump 34. The control devices and electrical components are suitably arranged as known in the art to accurately provide the

proper control and programming of the pressure and temperature over time needed to yield the composite materials of the present invention.

Referring to Figure 5B, an exploded cross sectional view high pressure unit 38 comprises anvils 45 and support rings 42, 43, and 44, container 36, and reaction cell 37 is shown for one embodiment of the present invention. The reaction cell 37 further comprises a graphite heater 47 which houses the sample material 48 used to make the composite material of the present invention. The upper and lower concentric rings 42, 43, and 44 are composed of pre-stressed steel rings, and the anvil 45 is composed of steel. A rubber ring 46 is disposed between the upper and lower concentric rings 42, 43, and 44 and the anvil 45. The container 36 serves as a pressure-transmitting medium, generating a near-hydrostatic stress in the reaction cell 37, and provides thermal and electrical insulation for the graphite heater 47. The reaction cell 37 forms the high temperature portion of the container 36, and is a graphite cylinder providing heater 47, in this example. The cylindrical graphite heater 47 is surrounded by container 49 composed of a deformable material in the form of plastic clay, for example. The cylindrical graphite heater 47 provides a path for the electrical current, whereas the top and bottom graphite parts 50 provides electrical contacts for the current. Clay spacers 51 and graphite separators 52 provide a disc-shaped volume for sample 48 inside reaction cell 37.

Accordingly, the disc-shaped sample material 48 tends to heat up uniformly via the flow of current through cylindrical graphite heater 47. The pressure in the



reaction cell 37 is calibrated via known phase transitions in solid substances, for example. These transitions are revealed by changes in electrical resistivity as a function of pressure. The temperature in the reaction cell is calibrated via known values of melting temperatures of different substances under high pressure. In  
5 reaction cell 37, the resistance sharply increases during melting of the metal used for calibration. In practice, the voltage across the reaction cell 37 is gradually increased and changes in the current are measured.

In Figure 5C, a more detailed and enlarged cross sectional view of the  
10 container 36 with the reaction cell 37 is shown for one embodiment of the present invention. The cylindrical container 49 provides a near isometric pressure on the material 48 of the sample to produce the composite material of the present invention. The force supplied by the hydraulic press (22, 26, 24, 34, 27, oil tank 20, 32, 23, 33) is converted into compressive pressure on the sample material 48, while the graphite  
15 heater 47 generates and maintains a sufficient temperature over a preset time period.

The versatility and applicability of this invention will become more apparent when the following examples are considered.

## EXAMPLES

### Example 1

#### Particle-strengthened Composite No. 1

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A 50:50 (wt.%) mixture of fullerenes and diamond powder (0.5  $\mu\text{m}$ ) was prepared by ball milling. A green body was shaped in a die under 0.5 GPa at room temperature. It was placed into the reaction cell of the high pressure-high temperature (HPHT) chamber and sintered at a pressure of about 3 GPa, at a  
10 temperature of about 800°C and for a holding time of about 1,000 seconds.

### Example 2

#### Particle-strengthened Composite No. 2

A 50:50 (wt.%) mixture of fullerenes and diamond powder (50  $\mu\text{m}$ ) was  
15 prepared by ball milling. A green body was shaped in a die under 1 MPa at room temperature. It was placed into the reaction cell of the high pressure-high temperature (HPHT) chamber and sintered at a pressure of about 3 GPa, at a temperature of about 800°C and for a holding time of about 1,000 seconds.

20

### Example 3

#### Particle-strengthened Composite No. 3

A 70:30 (wt.%) mixture of diamond (50  $\mu\text{m}$ ) and diamond (0.5 $\mu\text{m}$ )/fullerene powder was prepared by ball milling. A green body was shaped in a die under 0.1

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GPa at room temperature. It was placed into the reaction cell of the high pressure-high temperature (HPHT) chamber and sintered at a pressure of about 1 GPa, at a temperature of about 700°C and for a holding time of about 1,000 seconds.

5

#### Example 4

##### Particle-strengthened Composite No. 4

10

A 50:50 (wt.%) mixture of fullerenes and TiC powder (1  $\mu\text{m}$ ) was prepared by ball milling. A green body was shaped in a die under 0.1 GPa at room temperature. It was placed into the reaction cell of the high pressure-high temperature (HPHT) chamber and sintered at a pressure of about 1 GPa, at a temperature of about 900°C and for a holding time of about 100 seconds.

15

#### Example 5

##### Particle-strengthened Composite No. 5

As in Example 4, but using powders of c-BN, SiC or other carbides (boride),  
20 instead of TiC powder.

### Example 6

#### Fiber-strengthened Composite No. 1

A carbon fiber weave was infiltrated with pitch and carbonized at a pressure of about 0.1 GPa and at a temperature of about 700°C. The remaining open porosity in the composite material was infiltrated with mixed fullerenes at a pressure of about 0.1 GPa, and at a temperature of about 400°C. The nanostructured carbon binder phase was formed by sintering at a pressure of about 0.5 GPa, at a temperature of about 800°C, and for a holding time of about 1000 seconds.

### Example 7

#### Fiber-strengthened Composite No. 2

A carbon fiber fabric was bonded by chemical vapor infiltration (CVI), using a methane/hydrogen precursor at a temperature of about 1,000°C. The porous composite was infiltrated with pitch at 0.1 GPa, at a temperature of about 400°C, and transformed under pressure into a coke matrix at a pressure of about 0.1 GPa, at a temperature of about 700°C, for a holding time of about 10,000 seconds. The composite was thereafter heated in vacuum at 2500°C to graphitize the coke.

Example 8

Fiber-strengthened Composite No. 3

A porous C/C composite, as described in Example 7, was infiltrated with C<sub>60</sub> plus anthracene in the liquid state under a pressure of 0.1 GPa. The binder was carbonized at a pressure of about 1 GPa, and at a temperature of about 1000°C, for a holding time of about 1000 seconds. The composite was then heated in vacuum at 2500°C to accomplish thermal stabilization and removal of residual hydrogen.

Example 9

Network-strengthened Composite No. 1

A laminated titanium-mesh was infiltrated with mixed fullerenes at a pressure of about 0.1 GPa and at a temperature of about 400°C. The nanostructured carbon binder phase was formed by sintering at a pressure of about 1 GPa, and a temperature of about 1000°C, for a holding time of about 100 seconds.

Example 10

Network-strengthened Composite No. 2

A laminated steel-mesh structure (or any other metallic alloy wire structure) was infiltrated with mixed fullerenes, as described in Example 9. The nanostructured

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carbon binder phase was formed by sintering at a pressure of about 0.5 GPa, and a temperature of about 700°C, for a holding time of about 1,000 seconds.

#### Example 11

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##### Network-strengthened Composite No. 3

A porous titanium body was infiltrated with a 40:60 mixture of diamond powder (0.5 $\mu$ m) and fullerenes. The infiltration was executed at an infiltration pressure of about 0.1 GPa and at a temperature of about 400°C. The nanostructured carbon-diamond composite was formed by sintering at a pressure of about 1 GPa, and a temperature of about 1000°C, for a holding time of about 100 seconds.

#### Example 12

15

##### Network-strengthened Composite No. 4

A porous titanium body sintered on top of a bulk titanium substrate was infiltrated with a 60:40 mixture of fullerenes and TiC powder (1  $\mu$ m). The infiltration was carried out at an infiltration pressure of about 0.1 GPa, and a temperature of about 400°C. The composite matrix was then sintered at a pressure of about 0.5 GPa, and a temperature of about 700°C, for a holding time of about 1,000 seconds.

Example 13

Bicontinuous-strengthened Composite No. 1

A porous  $\text{Al}_2\text{O}_3$ ,  $\text{Al}_2\text{O}_3$ -base,  $\text{ZrO}_2$ ,  $\text{ZrO}_2$ -base, or other oxide ceramic,  
5 produced by incomplete sintering of nano- or micro-scale particles, was infiltrated  
with mixed fullerenes. The nanostructured carbon binder phase was formed by  
sintering at a pressure of about 0.5 GPa, and a temperature of about 700°C, for a  
holding time of about 1,000 seconds.

10

Example 14

Bicontinuous-strengthened Composite No. 2

15

A porous TiC, TiC-base, SiC, SiC-base or other carbide ceramic, produced by  
incomplete sintering of nano- or micro-scale particles, was infiltrated with mixed  
fullerenes. The nanostructured carbon binder phase was formed by sintering at a  
pressure of about 0.1 GPa, and a temperature of about 900°C, for a holding time of  
about 100 seconds.

20

Example 15

Bicontinuous-strengthened Composite No. 3

A porous  $\text{B}_4\text{C}$ ,  $\text{TiB}_2$ , or other boride ceramic, produced by incomplete sintering  
of nano- or micro-scale particles was infiltrated with mixed fullerenes. The

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nanostructured carbon binder phase was formed by pressure-assisted sintering, as in Example 14.

#### Example 16

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#### Bicontinuous-strengthened Composite No. 4

A porous graphitic C or diamond ceramic was infiltrated with mixed fullerenes. The nanostructured carbon binder phase was formed by pressure-assisted sintering, as in Example 14.

10

#### Example 17

#### Bicontinuous-strengthened Composite No. 5

15 A porous WC/Co, TiC/Ti, UC<sub>2</sub>/U, or other ceramic, produced by incomplete solid or liquid phase sintering of nano- or micro-scale particles was infiltrated with mixed fullerenes or a diamond/fullerene mixture. The nanostructured carbon binder phase was formed by pressure-assisted sintering, as in Example 14.

#### Example 18

20

A scaleable method was devised for the fabrication of a new class of carbon-ceramic composite materials of the present invention for applications in non-lubricated, thermally-resistant bearings. The composite materials were produced by



pressure-assisted sintering of mixtures comprising fullerene and diamond, or fullerene and graphite particle mixtures. The resulting composite materials were observed to exhibit reduced weight, good thermal stability, good radiation resistance, hardness comparable to hardened steel, exceptional resilience, frictional resistance  
5 lower than that of graphite or diamond, and excellent polishability, thus making them attractive candidates for use in bearing applications in space vehicles and platforms.

Attempts were made to develop composite rollers and sliding fits for fabricating precision bearings. To facilitate these attempts, procedures were  
10 developed for hot pressing the hard carbon-ceramic composite materials, and thereafter grinding the resulting materials into flat, round and spherical pieces. The pieces were then polished to yield bearings possessing a super-smooth surface finish. These attempts were made to produce bearings that would conform to specific performance requirements as dictated by producers of precision bearing.

15

As previously noted, Applicants have observed that a carbon binder mixture containing  $C_{60}$  fullerene fuses under pressures of from about 1 to 10 GPa at temperatures of from about 600°C to 1000°C to yield an amorphous carbon phase referred herein as "Diamonite-A" which exhibits a hardness value between that  
20 exhibited by silicon carbide and diamond. Applicants further observed that a carbon binder mixture containing mixed fullerene (i.e.,  $C_{60}$ ,  $C_{70}$ , and the like) fuses at lower pressures of from about 0.1 to 1.0 GPa to yield a different form of an amorphous

carbon phase referred herein as "Diamonite-B" which exhibits a hardness value between that exhibited by hardened steel and carbide.

A new class of composite materials was prepared using the mixed fullerene carbon binder mixture in combination with either diamond particles or graphite particles, respectively. Upon pressure sintering, the prepared composite materials comprising mixed fullerene carbon binder blended with a high fraction of diamond particles yielded a composite material referred herein as "Diamonite-C". Upon pressure sintering, the prepared composite materials comprising mixed fullerene carbon binder blended with a high fraction of graphite particles yielded a composite material referred herein as "Diamonite-D". The resulting composite materials exhibited excellent mechanical properties including high hardness, low friction and exceptional resilience. This combination of mechanical properties is unusual and atypical.

15

The Diamonite-C and -D were each produced by pressure-assisted sintering of mixed fullerene carbon binder phase in combination with diamond and graphite particles, respectively. In particular, Diamonite-C was prepared by ball milling mixed fullerene in an amount of about 60 percent weight with fine diamond particles, and sintering the resulting mixture at a pressure of about 2.0 GPa, and a temperature of about 800°C for about 1,000 seconds. Diamonite-D was prepared by ball milling mixed fullerene in an amount of about 60 percent weight with fine graphite particles, and sintering the resulting mixture at a pressure of about 0.3 GPa, and a

temperature of about 800°C for about 1,000 seconds. The properties of Diamonite-A, -B, -C, and -D are listed in Table 1 below. Applicants observed the high hardness of Diamonite-C, which is comparable to that of diamond, and the exceptional thermal stability of Diamonite-D.

5

Table 1

Material Properties	Diamonite-A	Diamonite-B	Diamonite-C	Diamonite-D
Precursor powder	C <sub>60</sub> Fullerene	Mixed fullerenes	Diamond and Mixed fullerenes	Graphite and Mixed fullerenes
Hardness, HV (GPa)	30-35	25-30	35-60	10-25
Density (g/cm <sup>3</sup> )	2.3-2.5	2.0-2.3	2.5-3.0	1.6-2.0
Specific strength (x10 <sup>6</sup> cm)	1.3-1.4	1.3-1.4	1.4-3.0	0.3-1.3
Thermal-stability (°C)	2000	3000	1200	3000
Resistivity (ohm*cm)	0.01-0.1	0.1-1	>1	0.001-0.01
Manufacturable pressure (GPa)	1-3	0.1-1	1-3	0.1-1
Manufacturable size (cm)	0.3-10	1-100	0.3-10	1-100

Because of the relatively high pressures needed to fuse and consolidate these mixtures, the maximum manufacturable size was about 10 cm for Diamonite-A and -C and about 100 cm for Diamonite-B and -D. This capability is, for example, more than sufficient for making preforms suitable for fabricating bearings of almost any desired size or shape.

A significant achievement has been the successful mechanical polishing of the composite materials of the present invention, which has permitted close

examination of microstructures and allowed hardness measurements to be performed.

Referring to Figure 6A, a representative micrograph of hardened polished  
5 steel having a Vickers hardness value of 7.6 GPa is shown. Hardness indentations  
were made in the steel material at loads of 100, 200, 300, 500, and 1,000 g,  
respectively. Referring to Figure 6B, a representative micrograph of a polished  
sample of Diamonite-C is shown. The surface of the Diamonite-C sample contained  
light and dark regions. The light regions are composed mostly of the carbon binder  
10 phase (i.e., Diamonite-B, or sintered mixed fullerene), and the dark regions are  
composed of Diamonite-C (i.e., sintered product of mixed fullerene and diamond  
particles). Such segregation of the corresponding phases is believed to be a result  
of incomplete mechanical mixing of the binder and the matrix phases, prior to hot  
pressing.

15

Measuring the Vickers hardness of the Diamonite-C composite material was  
difficult due to the inability to obtain well-defined indentations irrespective of the  
applied load. Referring back to Figures 6A and 6B, the clearly visible indentations of  
the hardened steel sample is more defined than the corresponding barely visible  
20 "cross-like" indentations in the mostly Diamonite-B regions of the Diamonite-C  
composite material. After several tests, utilizing different loads, it became clear that  
indenter-induced deformation in the Diamonite-B phase must have been almost  
entirely elastic in nature – except for a tiny plastically-deformed region formed by the

indenter tip. The Vickers hardness of the darker Diamonite-C composite was measured to be from about 35 to 64 GPa, whereas the Vickers hardness of the lighter Diamonite-B binder phase was measured to be from about 12 to 20 GPa. These results were in accord with independent hardness measurements (on Mohs  
5 scale) obtained by scratch tests, so that any uncertainty regarding the validity of the Vickers hardness data was thus removed.

The above observations, indicating that Diamonite-B phase is both hard and exceptionally resilient, prompted additional compression tests on small samples of  
10 pure Diamonite-B and Diamonite-C. These tests confirmed that Diamonite-C is stronger and stiffer than Diamonite-B, but fracture strains are comparable (about 2%) as shown in Figure 7. Moreover, Diamonite-C containing fine diamond particles in the range of from about 0.5 to 1.0  $\mu\text{m}$  has a somewhat higher fracture strain than the same material containing coarse diamond particles of from about 64 to 80  $\mu\text{m}$ . This  
15 raises issues concerning the influence of diamond particle size, distribution and volume fraction on the mechanical performance of Diamonite-C. Such experiments are now feasible, because of improvements made in the mixing of the starting materials (i.e., mixed fullerene and diamond particles) and the availability of sub-micron scale diamond powders, including shock-synthesized nano-diamond powder.  
20 The present work suggests that much higher hardness, bend strength and stiffness can be achieved in 30:70 (binder: matrix) to yield a Diamonite-C that is 100% composite with no segregation, while retaining a high work-to-fracture due to the resilience of the Diamonite-B binder phase. Recent work has also shown the

feasibility of fabricating carbon-fiber reinforced composite materials of the present invention by pressure-assisted sintering of mixed fullerene and chopped carbon fibers or mixed fullerene-infiltrated woven carbon fiber preforms.

5           Friction coefficients were determined using pin-on-disc and tilted-plane methods. In both tests, the measured dry friction coefficients for Diamonite-A and B, at rest and in motion, were measured to be lower than that of diamond, including diamond with a mirror-polished surface. Pin-on-disc friction experiments, performed on Diamonite-A, gave friction coefficients of 0.15 to 0.17 in humid air and 0.05 to  
10 0.12 in dry nitrogen. On the other hand, tilted-plane friction experiments, performed on Diamonite-A, gave values of 0.07 against steel, 0.12 against Teflon, and 0.07 against graphite. The commercial implications of these findings could be quite significant for bearing and sliding fit applications.

15           Although various embodiments of the invention have been shown and described, they are not meant to be limiting. Those of skill in the art may recognize various modifications to these embodiments, which modifications are meant to be covered by the spirit and scope of the appended claims.